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ABSTRACT

This booklet, one of a series of 17 developed at Prince George's Community College, Largo, Maryland, provides an individualized, self-paced undergraduate organic chemistry instruction module designed to augment any course in organic chemistry but particularly those taught using the text "Organic Chemistry" by Morrison and Boyd. The entire series of modules covers the first 13 chapters of the Morrison-Boyd text in great detail. Each module has been provided with from one to three audiotapes, available from Prince George's Community College, to provide students additional explanations of particular concepts. Each module includes a self-evaluation exercise, a reference guide, worksheets to be completed with the audiotapes, answer sheets for the worksheets, a progress evaluation, an answer sheet for the progress evaluation, an answer sheet for the self-evaluation exercise, an introduction to the topic covered by the module, and student performance objectives for the module. The topic of this module is alkenes-reactions: dimerization, alkylation, and halogenation. (SL)

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ORGANIC CHEMISTRY

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V. Zdravkovich

9

Self

Instructional

Package

ALKENES-REACTIONS 1

ISE 021 580

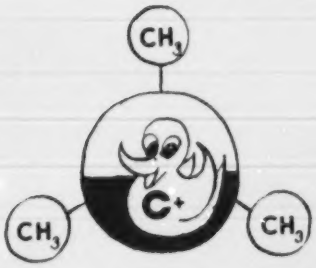
Self Instructional Sequence in

ORGANIC CHEMISTRY

"Copr.," V. Zdravkovich 1976

ALKENES - REACTIONS

DIMERIZATION, ALKYLATION AND HALOGENATION

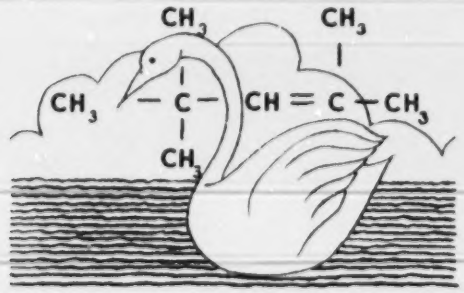


You are probably familiar with the famous story "The Ugly Duckling" by Hans Christian Andersen. This is a similar very short story told in the language of an organic chemist.

Once upon a time there lived a father, Isobutene, a mother, Isobutene, and a little Tertiary Butyl Carbonium Ion or TBCI. He used to be called T-Bic. Needless to say, T-Bic would not have even existed without the essential presence of the acidic godmother. He was a hyperactive child and on his road to adulthood he used to get into all kinds of trouble. T-Bic used to fight with the friendly Water, the neighborhood bully Isobutane and his little neighbor Sodium Chloride. All these side interactions did not prevent him from growing up. Like the ugly duckling who changed into a swan, T-Bic changed into -

_____.

After you have listened to the tape and completed the assignments on this work sheet, you will be able to tell what T-Bic changed into and also what were the results of all his childhood interactions.



Self Instructional Package No. 9
Form A - List of Objectives

ALKENES - REACTIONS I

ELECTROPHILIC ADDITION REACTIONS

DEFINITIONS -

The student will be able to define, explain and illustrate with appropriate examples where applicable the following terms: MARKOVNIKOV'S RULE, NUCLEOPHILE, ELECTROPHILE, HALOHYDRIN, DIMER, POLARIZATION, HYDRATION, HYDROHALOGENATION, ALKYL HYDROGEN SULFATE, DIMERIZATION, ALKYLATION, HALOGENATION.

REACTION MECHANISMS -

The student will be able to write the step by step mechanism for HYDRATION, HYDROHALOGENATION, ADDITION OF H_2SO_4, DIMERIZATION, ALKYLATION, HALOGENATION and any other electrophile addition reaction.

The student will be able to predict the major product in the electrophilic reactions enumerated above and explain this on the basis of the mechanism.

The student will be able to predict the orientation in a given electrophile addition reaction on the basis of the mechanism.

The student will be able to predict the relative reactivities of different alkenes in different electrophilic addition reactions.

The studentwill be able to predict and explain the rearrangements observed in different electrophilic addition reactions.

MULTI-STEP SYNTHETIC SCHEMES

The student will be able to devise multi-step synthesis schemes for the synthesis of an alcohol, an alkyl halide, a vicinal dihalide, an alkyl hydrogen sulfate, an alkene or alkane from methane or any other small alkane.

The student will be able to identify all the reagents in a given multi-step synthesis scheme.

The student will be able to identify i.e. draw the structures and name all the compounds in a given multi-step sunthesis scheme.

Self Instructional Package No. 9
Form B - Self Evaluation Exercise

ALKENES - REACTIONS I

ELECTROPHILIC ADDITION REACTIONS

Identify the statements below as true or false by placing a capital F or T in the space provided.

1. _____ In the first step of an electrophilic addition reaction mechanism alkene serves as a nucleophile.

2. _____ In the first step of an electrophilic reaction mechanism H positive ion abstracts one π electron from the alkene to form a bond.

3. _____ The intermediate species in the electrophilic reaction mechanism is the carbonium ion.

4. _____ The carbonium ion in the hydration reaction reacts with the hydroxide ion and yields an alcohol.

5. _____ The carbonium ion formed in Step 1 of the alkylation reaction abstracts a hydride ion from the alkane.

6. _____ The carbonium ion formed in Step 1 of the dimerization reaction reacts with another molecule of alkene.

7. _____ The alkene molecule in the dimerization serves a nucleophile in Step 2 of the mechanism.

8. _____ When isobutene reacts with hydrogen bromide, bromine adds to the doubly bonded carbon that hold more hydrogens.

9. _____ Isobutene reacts with concentrated sulfuric acid to produce an alkyl hydrosulfate which will change into an alcohol when heated with water.

10. _____ Isobutene is more reactive than 2-butene toward an electrophilic addition reaction.

11. _____ 2-methyl-2-pentene is less reactive toward acid tha 2,3-dimethyl-2-pentene.

12. _____ A halohydrin is a compound that contains halogen and OH group on the vicinal carbon atom.

13. _____ Isobutene reacts with 63% H_2SO_4 as compared to propene that reacts with 80% H_2SO_4 and ethylene that reacts with 98% H_2SO_4. This clearly indicates that ethylene is most reactive and that isobutene is least reactive.

14. _____ The compound or compounds formed in the reaction of 2-methyl-2-pentene with bromine in aqueous solution is/are:

a) 2-bromo-2-pentanol

b) 2,3-dibromo-2-methyl pentane

c) 3-bromo-2-methyl-2-pentanol

d) 2-bromo-2-methyl-3-pentanol

15. _____ When isobutene is heated in presence of an acid the following product is/are formed:

a) t-butyl carbonium ion

b) 2,2,4-trimethyl pentane

c) 2,4, 4-trimethyl-2-pentene

d) 2,4,4-trimethyl-1-pentene

16. _____ When isobutene reacts with bromine in aqueous solution with sodium chloride present the following compound is/are formed:

a) 1,2-dibromo-2-methyl propane

b) 1-chloro-2-bromo-2-methyl propane

c) 1-bromo-2-methyl-2-propanol

d) 1-bromo-2-chloro-2-methyl propane

17. _____ Identify the major product A in the reaction below -

3-methyl-2-pentanol $\xrightarrow{\text{acid}}$ 2-methyl-3-pentane $\longrightarrow$ A

a) 3,4,5-trimethyl-5-ethyl-3-heptene

b) 3,4-dimethyl-3,4-diethyl hexane

c) 3,4,5-trimethyl-3-ethyl heptane

d) 3,8-dimethyl-decane

18. _____ The major product in the acid catalyzed addition of water to 3,3-dimethyl-1-hexene is:

a) 3,3-dimethyl-1-hexanol

b) 3,3-dimethyl-2-hexanol

c) 2,3 dimethyl-2-hexanol

d) 2,3-dimethyl-3-hexanol

19. _____ The major product in the hydroiodination of 3,4,4-trimethyl-1-pentene is:

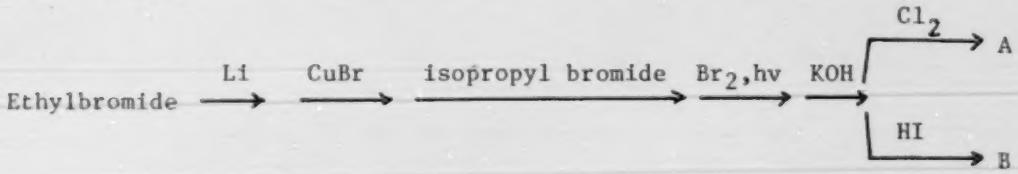
a) 2-iodo-3,4,4-trimethyl pentane

b) 2-iodo-2,3,4-trimethyl pentane

c) 3-iodo-3,4,4-trimethyl pentane

d) 3-iodo-2,3,4-trimethyl pentane

20. _____ Identify compounds A and B in the multi-step synthetic scheme below.



	A	B
a)	2,3-dichloro-2 methyl butane	2-iodo-3-methyl butane
b)	2,3-dichloro-2-methyl butane	2-iodo-2-methyl butane
c)	2,3-dichloro-2-butene	2-iodo butane
d)	1,2-dichloro propane	2-iodo propane

21. _____ Identify the reagents required for the laboratory synthesis of 4-bromo-3,4-dimethyl-3-hexanol for 2-bromo butane

a) Na, H_2O, Br_2,hv

b) Na, Br_2,hv, KOH, Br_2, H_2O

c) KOH, Acid, Br_2,hv, KOH, Br_2, H_2O

d) Li, CuBr, 2-bromo butane, Br_2,hv, KOH, Br_2, H_2O

Self Instructional Package No. 9
Form C - Reference Guide

ALKENES - REACTION I

ELECTROPHILIC ADDITION REACTIONS

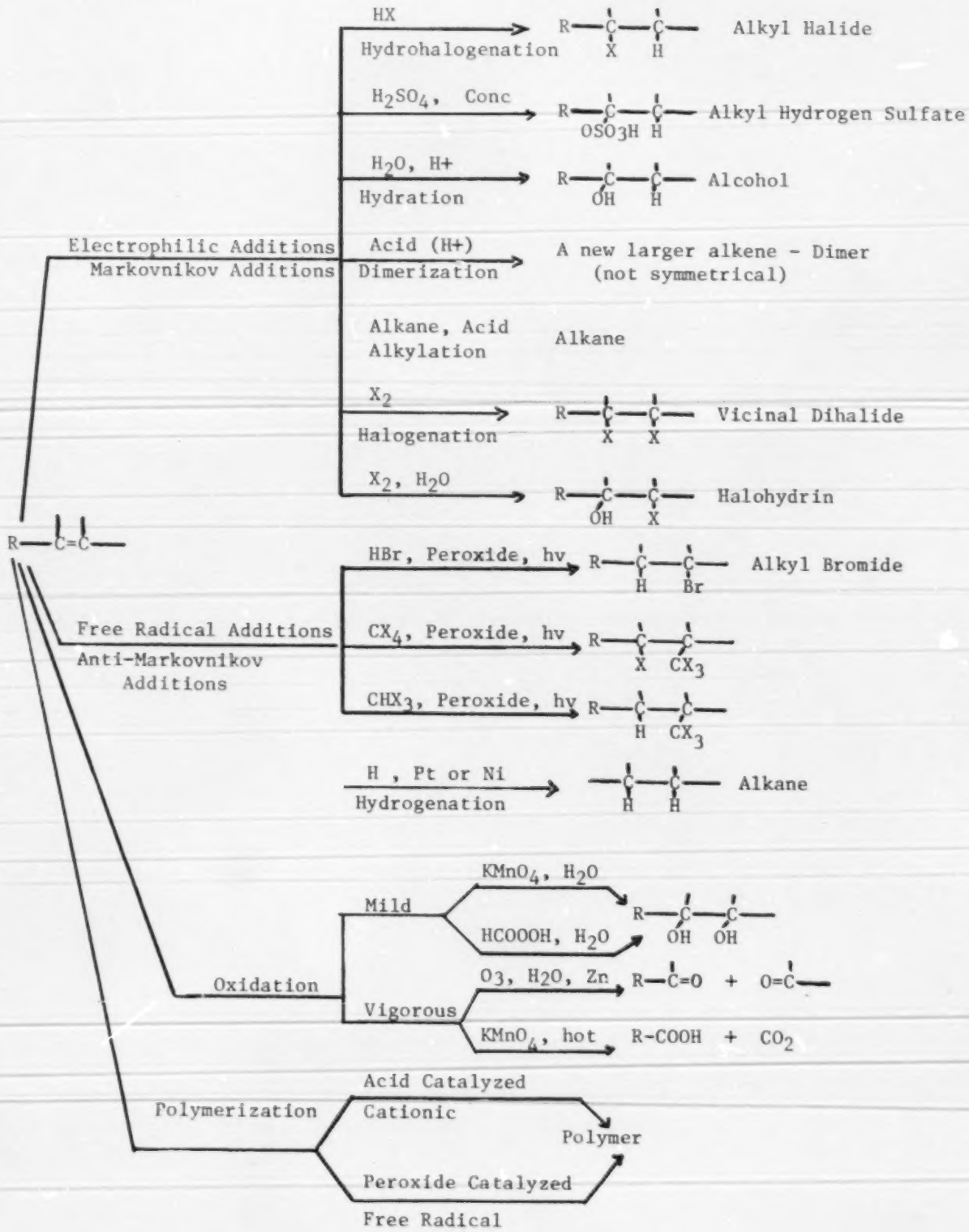
The Reference Guide should be used in conjunction with Form B or the Self Evaluation Exercise. The references provide the correlation between the questions in Form B and the available material in the text-book and in the form of tapes.

Questions 1,2,3,4	Chapter 6, Section 2,10,11	Morrison & Boyd Organic Chemistry
Questions 20,21	Chapter 6, Section 12	
Questions 5,17	Chapter 6, Section 16	
Questions 6,7,15	Chapter 6, Section 15	
Question 8	Chapter 6, Section 6	
Questions 9,13	Chapter 6, Section 8	
Questions 10,11	Chapter 6, Section 11	
Questions 12,14,16	Chapter 6, Sections 13,14	
Questions 19,20	Chapter 3, Sections 17,19,21 Chapter 5, Sections 12,14 Chapter 6, Sections 5,6,13,14,15,9	

For Questions 1,2,3,4,8,9,10,11,13,19,20,21, additional explanations and examples are provided in TAPE 1 - titled Additions of HX, H_2SO_4 and H_2O to alkenes, with the accompanying worksheet and answer sheet.

For Questions 5,6,7,12,14,15,16,17,18, additional explanations and examples are provided in TAPE 2, titled Dimerization, Alkylation and Halogenation, with the accompanying worksheet and answer sheet.

ALKENES - REACTIONS



However much thou art read in theory, if thou hast no practice thou art ignorant.

Gulistan (1258)

Self Instructional Package No. 9
Tape 1 - Worksheet

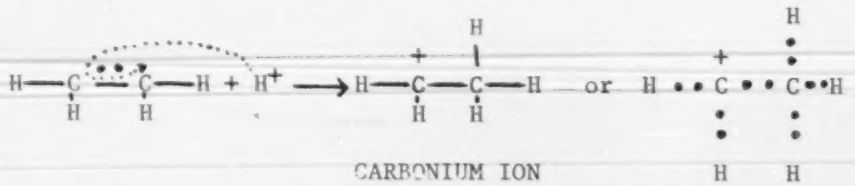
ALKENE - REACTIONS

ELECTROPHILIC ADDITION REACTIONS OF

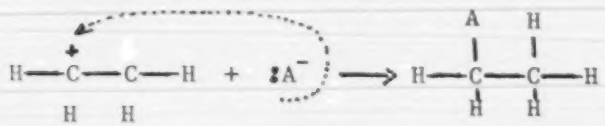
HBr, H_2SO_4 and H_2O TO ALKENES

Example No. 1

Step 1 - Addition of H+ to alkene and formation of the carbonium ion

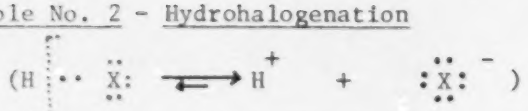


Step 2 - Reaction of the carbonium ion with the nucleophilic reagent

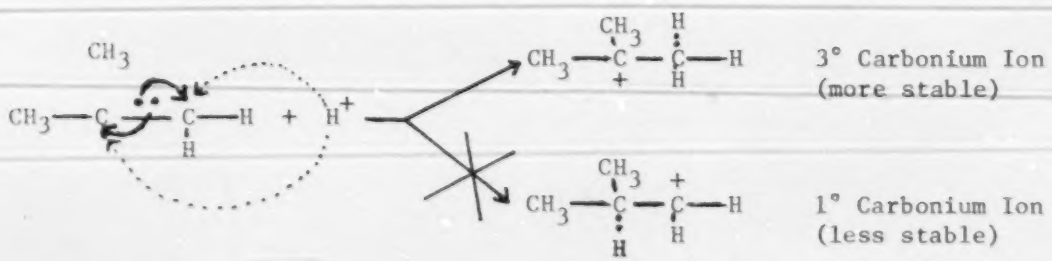


Electrophile Nucleophile

Example No. 2 - Hydrohalogenation



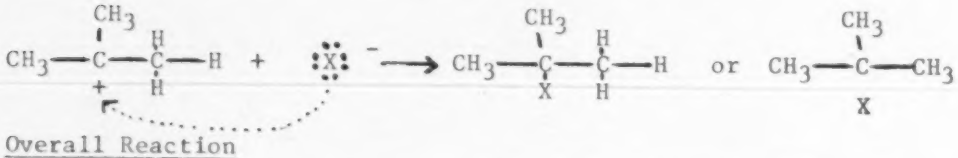
Step 1 - Formation of the Carbonium Ion



SIP No. 9 - Tape 1 Worksheet

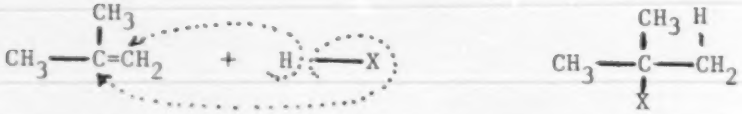
Example No. 2 - Hydrohalogenation (continued)

Step 2 - Reaction of the carbonium ion with the halid anion



Overall Reaction

OR



ASSIGNMENT NO. 1 - ADDITION OF SULFURIC ACID

Write the step by step mechanism for the addition of sulfuric acid to 2-methyl-2-butene. Identify all species as nucleophilic or electrophilic. Also write the overall reaction.

SIP No. 9 - Tape 1 Worksheet

ASSIGNMENT NO. 2

Write the step by step mechanism for the addition of hydrogen bromide to 3-methyl-1-butene that will account for the formation of 2-bromo-2-methyl-butane.

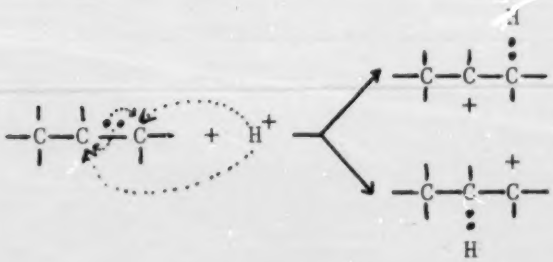
ASSIGNMENT NO. 3

Saturated Sam was asked to write the overall reaction and the step by step mechanism for the addition of HYDROGENCHLORIDE to 3,3-DIMETHYL-1-PENTENE. His answer incomplete and only partially correct is given below. Supply all the necessary corrections and/or additions.

SIP No. 9 - Tape 1 Worksheet

Example No. 3 - HYDRATION

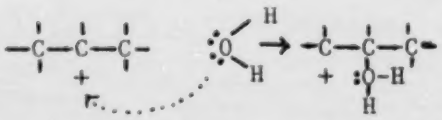
Step 1 - Formation of the Carbonium Ion



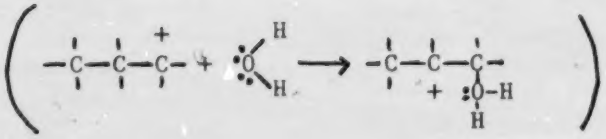
2° Carbonium Ion

1° Carbonium Ion

Step 2 - Reaction of the Carbonium Ion with the Nucleophile

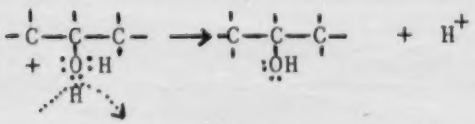


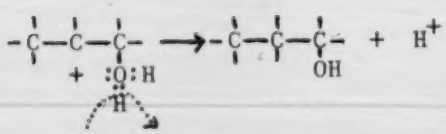
Protonated Alcohol
(Oxonium Ion)



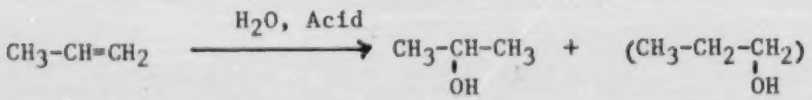
Protonated Alcohol
(Oxonium Ion)

Step 3 - Regeneration of the Catalyst





Overall Reaction



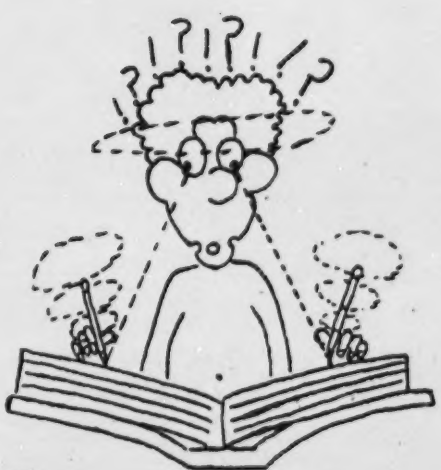
Small Percentage

SIP No. 9 - Tape 1 Worksheet

ASSIGNMENT NO. 4

Write the step by step mechanism and the overall reaction for the hydration of 3-Methyl-1-Pentene

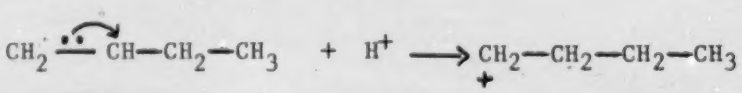
ASSIGNMENT NO. 5



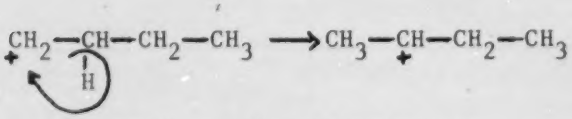
Confused Clyde was asked to write the step by step mechanism for the hydration of 1-Butene. His answer is given below. Examine his answer and make any necessary corrections.

$(H_2O \rightleftharpoons H^+ + OH^-)$

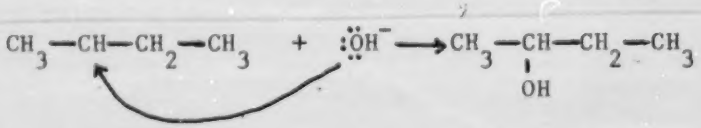
Step 1 - Formation of the carbonium ion



Rearrangement - stabilization of the carbonium ion



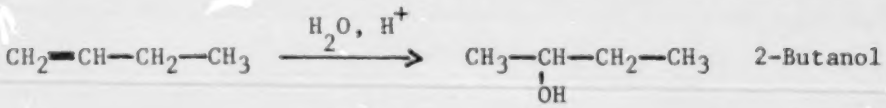
Step 2 - Reaction of the carbonium ion



SIP No. 9 - Tape 1 Worksheet

Assignment No. 5 - Step 2 (continued)

Overall Reaction:

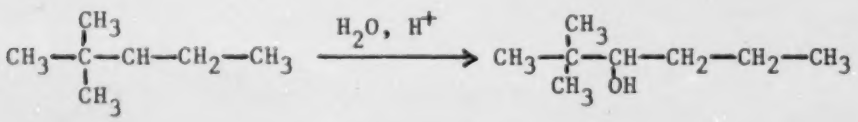


2-Butanol

ASSIGNMENT NO. 6

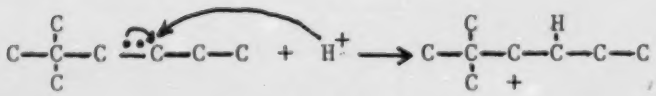
Forgetful Frieda was asked to write the step by step mechanism for the hydration of 2,2-Dimethyl-3-Hexene. Her answer is given below. Compete her answer and add the part that Frieda has forgotten.

Overall Reaction:



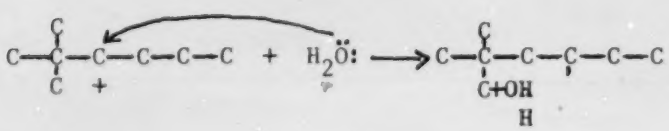
2,2-Dimethyl-3-Hexanol

Step 1



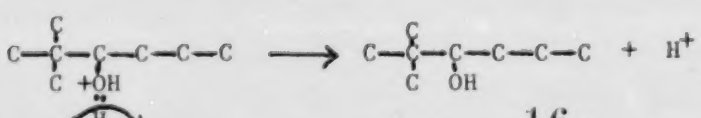
Carbonium Ion

Step 2



Protonated Alcohol

Step 3



SIP No. 9 - Tape 1 Worksheet

ASSIGNMENT NO. 7

Draw the structure and name the major product in the reactions below. (You are not asked to write the step by step mechanism although it is not prohibited.)

2-Methyl Propene $\xrightarrow{HBr}$

Propene $\xrightarrow{H_2SO_4}$

2-Methyl-2-Pentene $\xrightarrow{H_2O,\ Acid}$

3,3-Dimethyl-1-Butene $\xrightarrow{HI}$

3-Methyl-1-Pentene $\xrightarrow{H_2O,\ H^+}$

Example No. 4

MARKOVNIKOV'S RULE: In the ionic addition of an acid to the unsymmetrical carbon-carbon double bond of an alkene, the hydrogen of the acid attaches itself to the carbon atom that already holds the greater number of hydrogens.

ASSIGNMENT NO. 8

Which alkene of each pair would you expect to be more reactive toward addition of sulfuric acid. Why?

a) I 2-Methyl-1-Butene II 2,3-dimethyl-2-butene

b) I Propene II 2-Pentene

c) I Ethylene II 2-Butene

d) I 2-Methyl-2-Pentene II 3-Methyl-1-Pentene

e) I 2-Chloro-2-Butene II 2-Butene

f) 3-Bromo-2-Pentene II 2-Bromo-2-Pentene

SIP No. 9 - Tape 1 - Worksheet

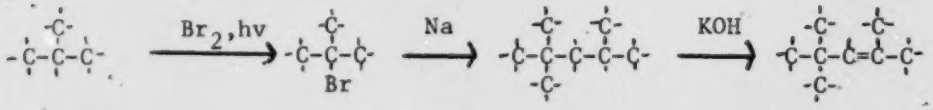
ASSIGNMENT No. 9

Identify all the steps in the laboratory synethesis of:

2-methyl-2-butanol and 2-Iodo-2,3-dimethyl butane from Propane

ASSIGNMENT NO. 10

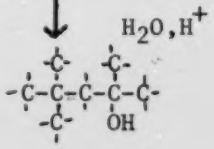
Saturated Sam was asked to identify all the steps in the laboratory synthesis of 2,4,4-Trimethyl-2-Pentanol from 2-Methyl Propane. His answer is given below. Examine his answer and make all the necessary corrections.



2-Bromo-2-Methyl Propane

2,2,4-Trimethyl Pentane

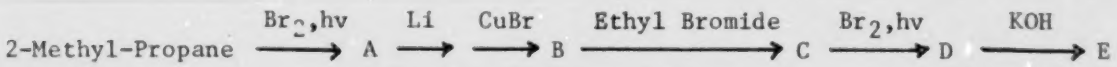
2,4,4-Trimethyl-2-Pentene

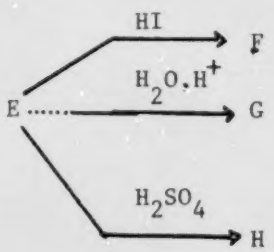


SIP No. 9 - Tape 1 - Worksheet

ASSIGNMENT NO. 11

Identify (draw the structure and name) compounds A through H in the reaction given below.



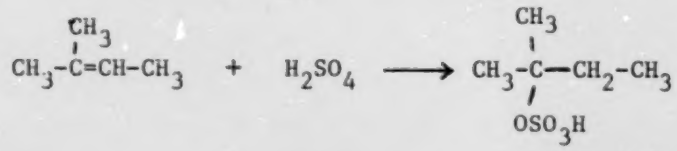


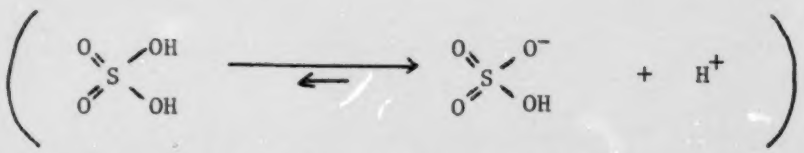
Self Instructional Package No. 9
Tape 1 - Answer Sheet

ELECTROPHILIC ADDITION REACTIONS OF HBr, H_2SO_4 and H_2O TO ALKENES

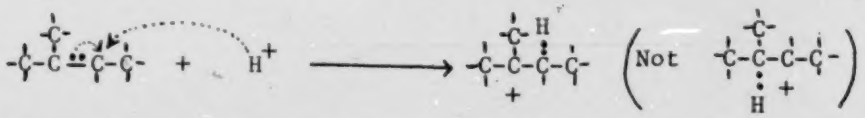
Assignment No. 1 - Addition of Sulfuric Acid

Overall Reaction



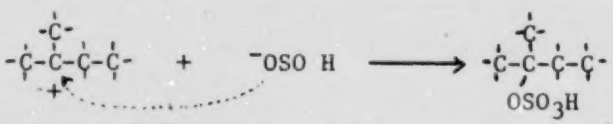


Step 1 - Formation of the Carbonium Ion (Rate determining step)



Nucleophile Electrophile

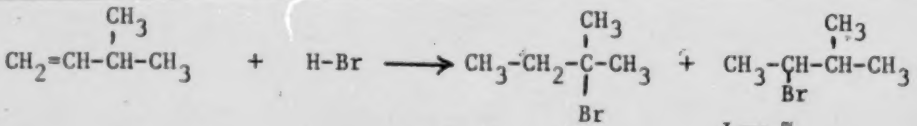
Step 2 - Reaction of the Carbonium Ion with the Nucleophile



Electrophile Nucleophile

Assignment No. 2

Overall Reaction:

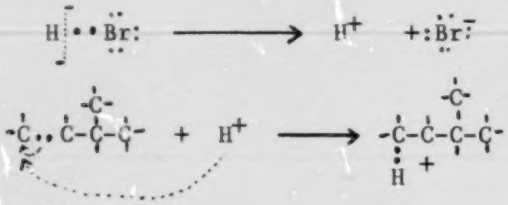


Low %

SIP No. 9
Tape 1 - Answer Sheet

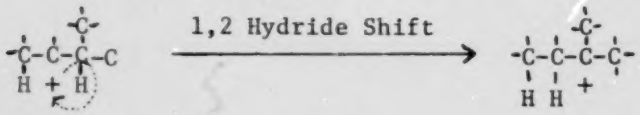
Assignment No. 2 (continued)

Step 1 - Formation of the Carbonium Ion



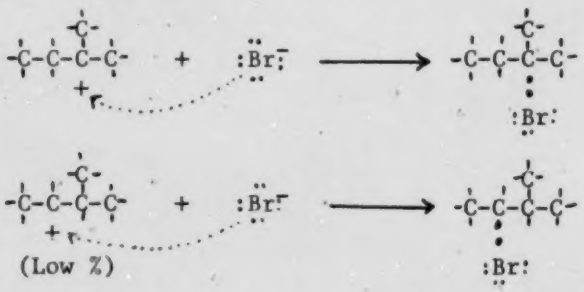
2° Carbonium Ion

Rearrangement or the Stabilization of the Carbonium Ion



3° Carbonium Ion

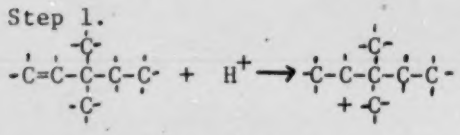
Step 2 - Reaction of the Carbonium Ion with the Bromide Anion



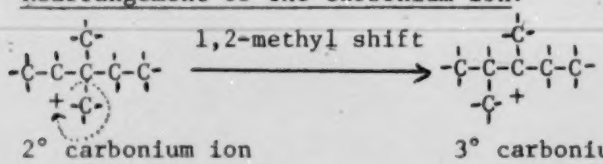
Assignment No. 3

Saturated Sam omitted the rearrangement of the carbonium ion.

Step 1.



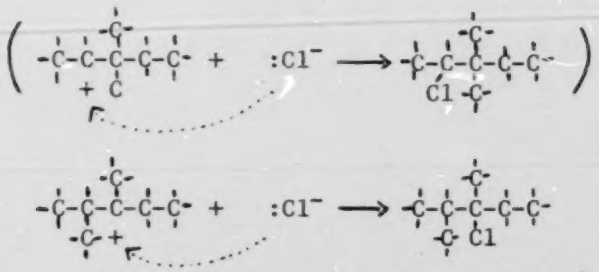
Rearrangement of the carbonium ion:



SIP No. 9
Tape 1 - Answer Sheet

Assignment No. 3 (continued)

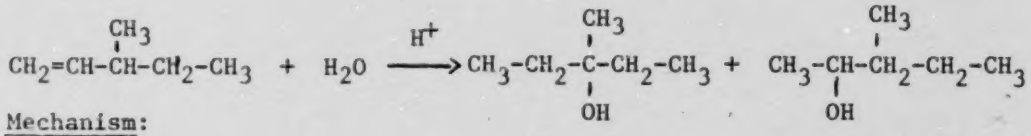
Step 2



3-Chloro-2,3-dimethyl pentane

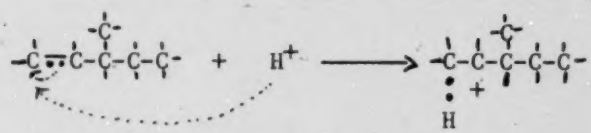
Assignment No. 4

Overall:

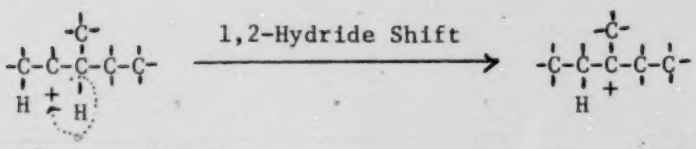


Mechanism:

Step 1 - Formation of the carbonium ion



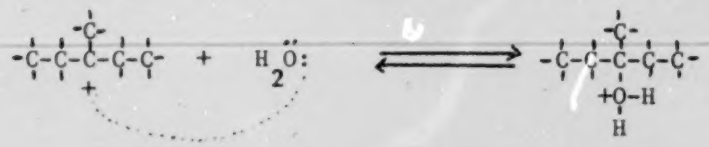
Rearrangement of the carbonium ion



2° carbonium ion

3° carbonium ion

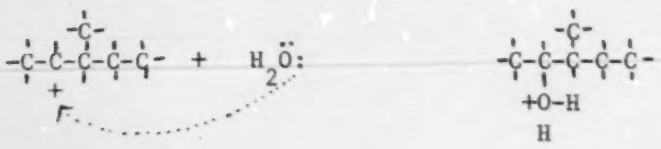
Step 2 - Addition of water to the carbonium ion



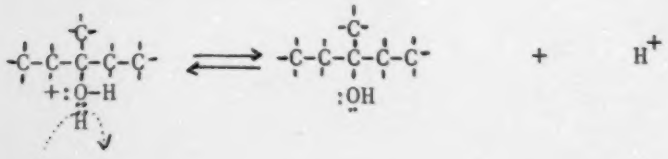
SIP No. 9
Tape 1 - Answer Sheet

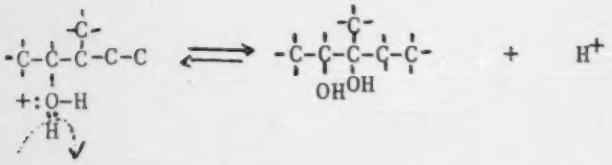
Assignment No. 4 (continued)

Step 2 - Addition of water to the carbonium ion (continued)



Step 3 - Regeneration of the catalyst





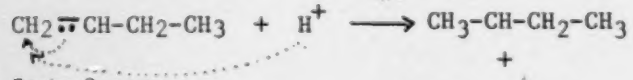
Assignment No. 5

($H_2O \rightleftharpoons H^+ + OH^-$ NOT correct) - There is virtually no dissociation of water

Step 1

($CH_2{=}CH\text{-}CH_2\text{-}CH_3 + H^+ \longrightarrow \overset{+}{C}H_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$ NOT correct)

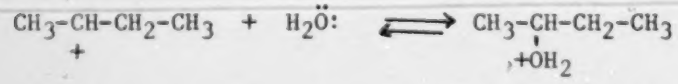
H^+ ion will add to the first C to produce a more stable secondary carbonium ion



Step 2

($CH_3\text{-}\overset{+}{C}H\text{-}CH_2\text{-}CH_3 + OH^- \longrightarrow CH_3\text{-}\underset{OH}{C}H\text{-}CH_2\text{-}CH_3$ NOT correct)

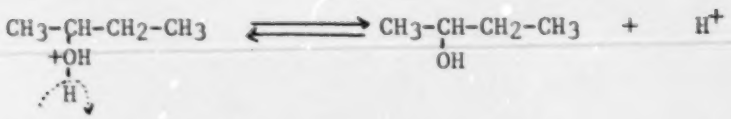
There are NO hydroxide ions in the mixture. Neutral water molecules serve as the nucleophile in Step 2.



Protonated Alcohol

SIP No. 9
Tape 1 - Answer Sheet

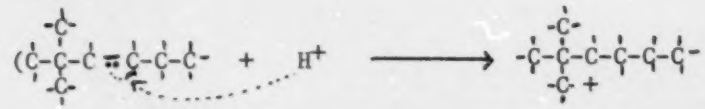
Step 3 - Regeneration of the catalyst



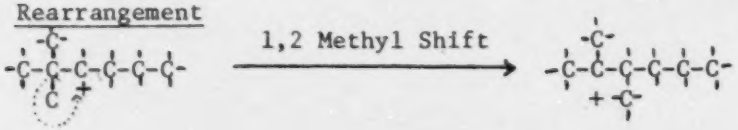
Assignment No. 6

Carbonium ion formed in the first step is a secondary carbonium ion, Frieda forgot to include the rearrangement of the carbonium ion which results in the formation of a more stable carbonium ion and consequently in a formation of a different alcohol.

Step 1

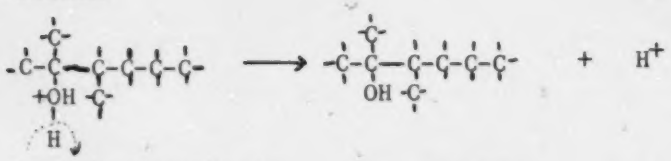


Rearrangement

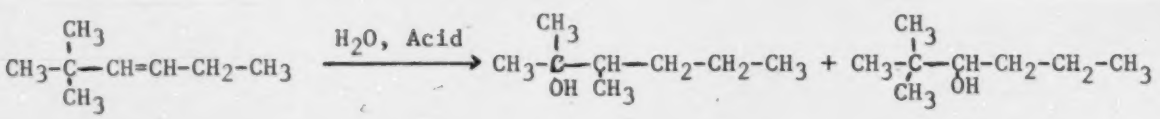


Step 2

Step 3

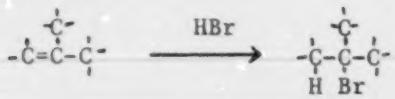


Overall Reaction:

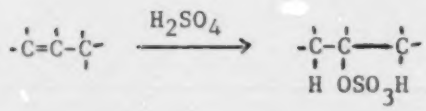


SIP No. 9
Tape 1 - Answer Sheet

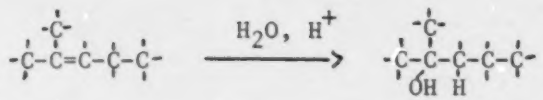
Assignment No. 7



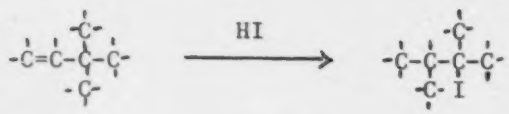
2-bromo-2-methyl propane



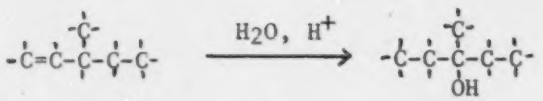
isopropylbisulfate



2-methyl-2-pentanol



2-Iodo-2,3-dimethyl butane



3-methyl-3-pentanol

Assignment No. 8

More reactive in each pair:

a) II

b) II

c) II

d) I

e) I

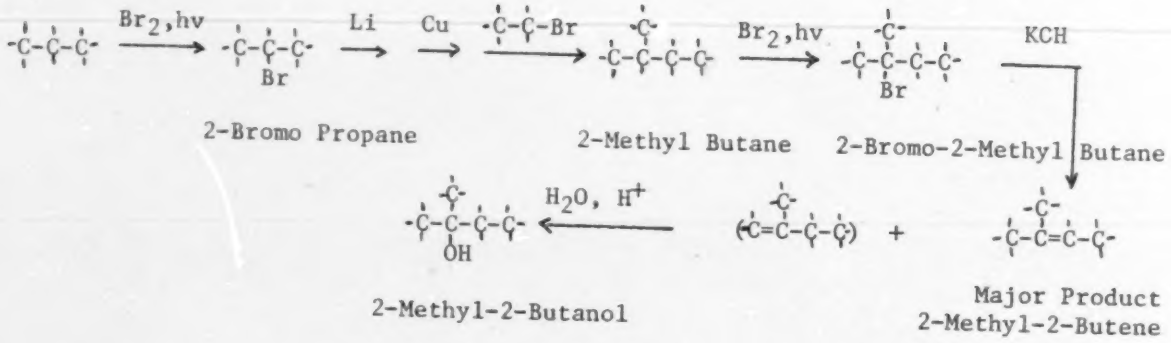
f) II

Explanation: Branching in a) b) c) d) and the possibility of the formation of the more stable intermediate carbonium ion. The electron withdrawing effect of halogen atom in e) and f) destabilizes the intermediate carbonium ion.

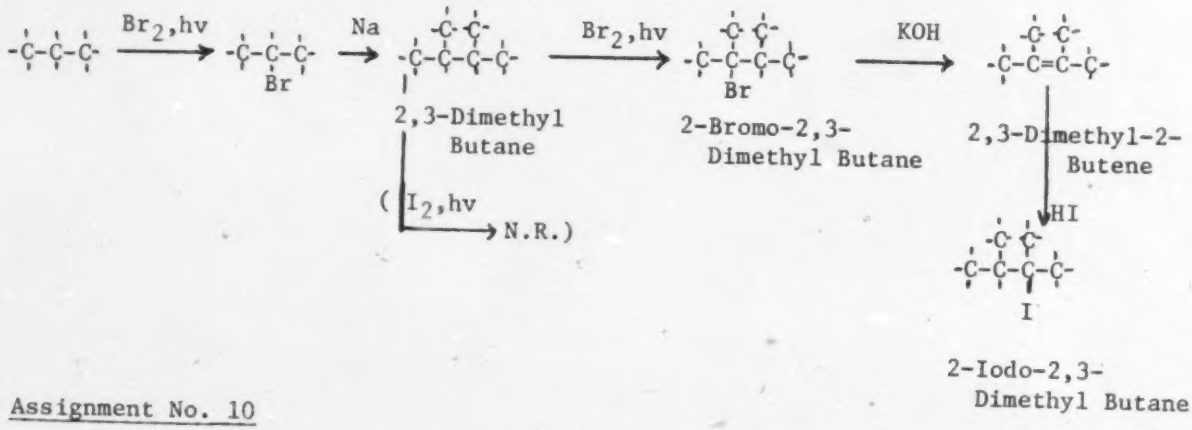
SIP No. 9
Tape 1 - Answer Sheet

Assignment No. 9

a)

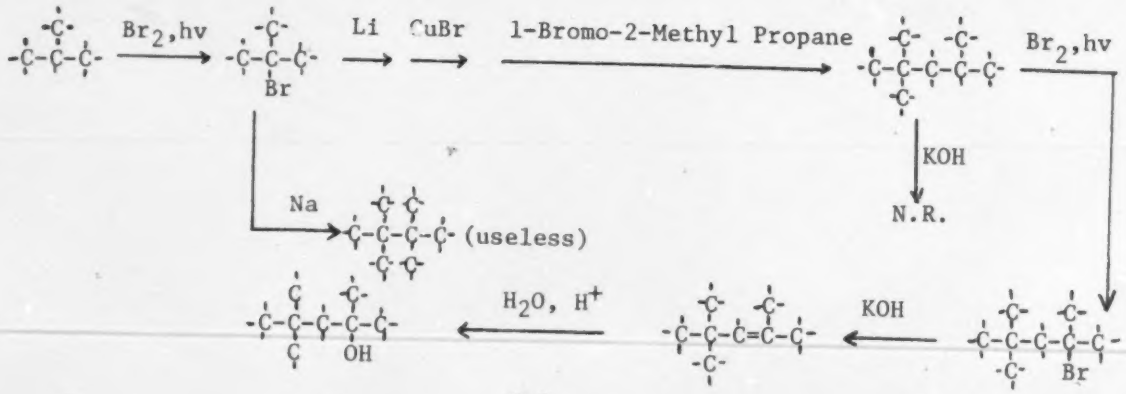


b)



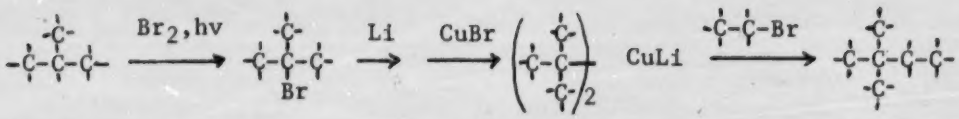
Assignment No. 10

Correct Pathway:



SIP No. 9
Tape 1 - Answer Sheet

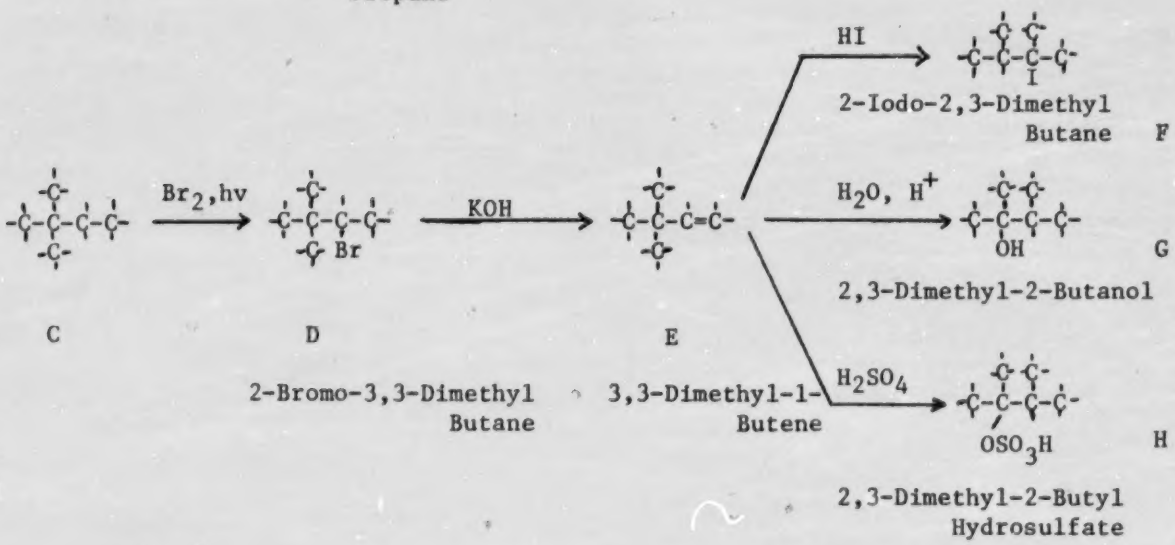
Assignment No. 11



A — 2-Bromo-2-Methyl Propane

B

C — 2,2-Dimethyl Butane



C

D — 2-Bromo-3,3-Dimethyl Butane

E — 3,3-Dimethyl-1-Butene

F — 2-Iodo-2,3-Dimethyl Butane

G — 2,3-Dimethyl-2-Butanol

H — 2,3-Dimethyl-2-Butyl Hydrosulfate

Self Instructional Package No. 9
Tape 2 - Worksheet

In order that knowledge be properly digested, it must have been swallowed with a good appetite.
Anatol France (1881)

ALKENES - REACTIONS

DIMERIZATION, ALKYLATION AND HALOGENATION

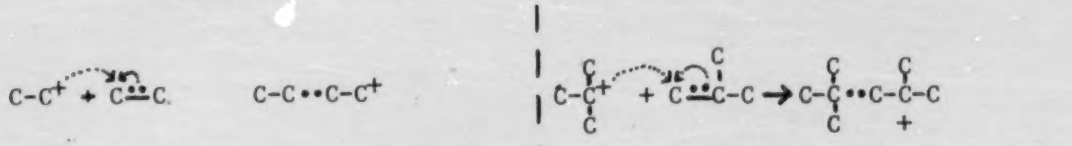
Example No. 1 - Dimerization Mechanism

Ethylene

2-methyl propene (isobutylene)

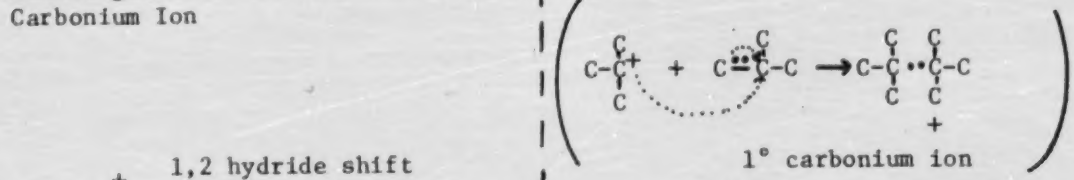
Step 1 - Addition of H^+ and formation of the Carbonium Ion

Step 2 - Reaction of the Carbonium Ion with Alkene to yield a new carbonium ion

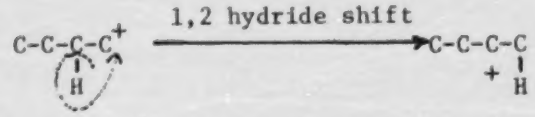


3° carbonium ion

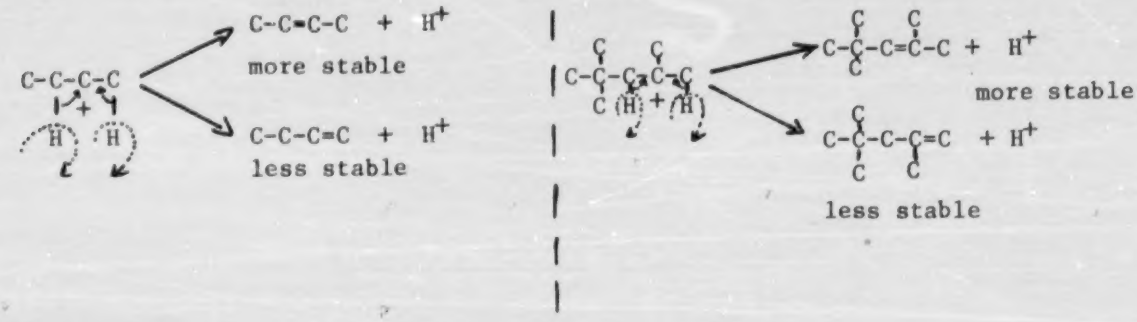
Rearrangement - Stabilization of the Carbonium Ion



1° carbonium ion



Step 3 - Repulsion of H^+ and formation of the double bond



more stable

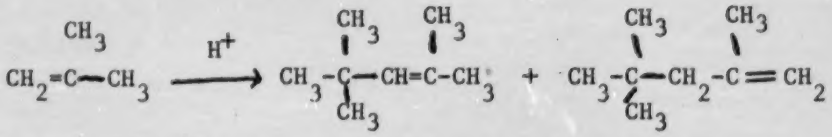
less stable

SIP No. 9
Tape 2 - Work Sheet

Overall reactions

Ethylene: $CH_2=CH_2 \xrightarrow{H^+} CH_3-CH=CH-CH_3 + CH_3-CH_2-CH=CH_2$

2-Methyl Propene:



Assignment No. 1

Write the step by step mechanism for the acid catalyzed dimerization of propene and 2-methyl-2-butene.

SIP No. 9
Tape 2 - Worksheet

Assignment No. 2

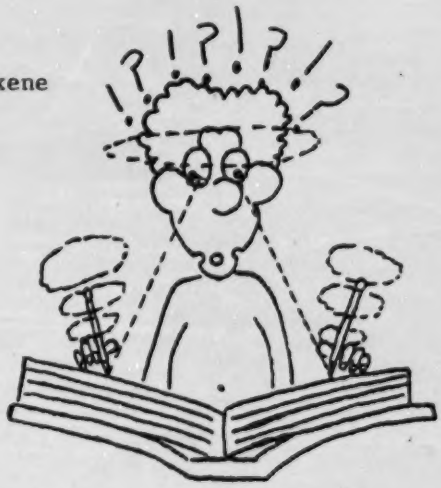
Inert Irma was asked to complete a number of reactions. Her answer is given below. Examine it and make any necessary corrections.

a) 2-methyl-1-butene $\xrightarrow{\text{acid}}$ 3,3,4-trimethyl-2-heptene

b) 2-butene $\xrightarrow{\text{acid}}$ 3,4-dimethyl-1-hexene + 3,4-dimethyl-2-hexene

c) 1-butene $\xrightarrow{\text{acid}}$ 3,4-dimethyl-3-hexene

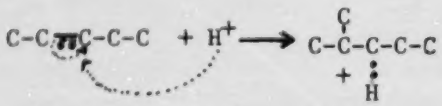
d) 2-methyl propene $\xrightarrow{\text{acid}}$ 2,5-dimethyl-3-hexene



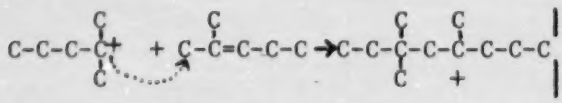
Assignment No. 3

Confused Clyde was asked to: a) write the step by stpe mechanism, b) identify the rate determining step, and c) write the overall reaction for the acid caralyzed dimerization of 2-methyl-2-penteneand 1-butene. Examine his answer carefully and make any necessary corrections.

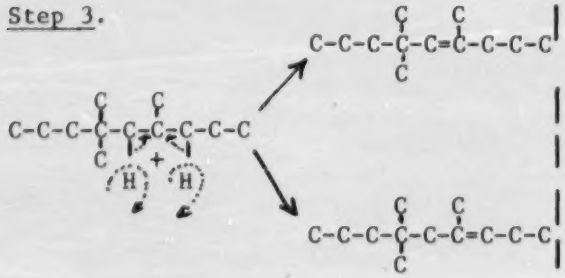
Step 1.



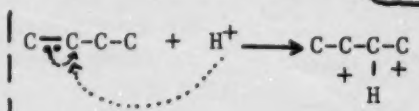
Step 2.



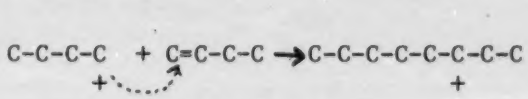
Step 3.



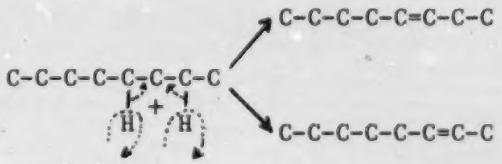
Step 1.



Step 2.



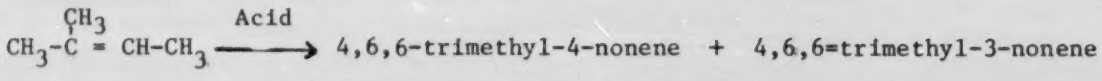
Step 3.

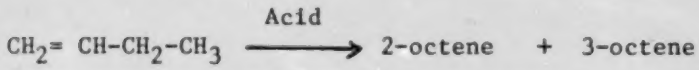


SIP No. 9
Tape 2 - Worksheet

Assignment No. 3 (continued)

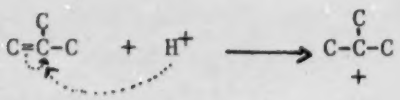
Overall reactions:



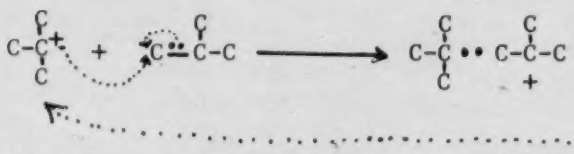


Example No. 2 - Alkylation Mechanism

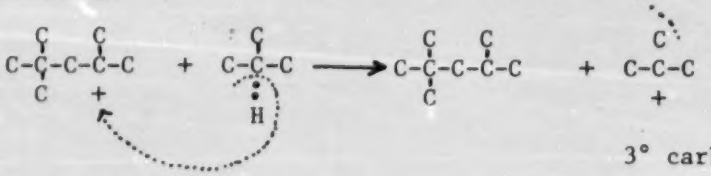
Step 1. - Addition of the H^+ to the double bond and the formation of the carbonium ion



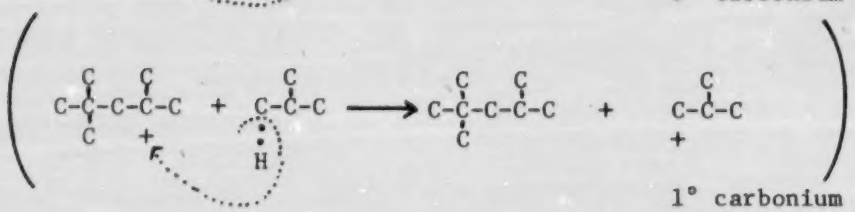
Step 2 - Addition of the carbonium ion to the alkene



Step 3 - Abstraction of the hydride anion from the alkane



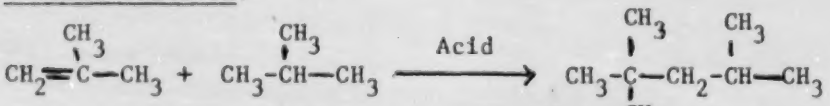
3° carbonium ion



1° carbonium ion

Steps 2,3 2,3 2,3 2,3

Overall reaction:



SIP No. 9
Tape 2 - Worksheet

Assignment No. 4

Write the step by step mechanism for the acid catalyzed reaction of propene with propane.

Assignment No. 5

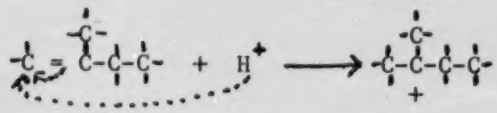
Write all the reactions of the carbonium ion introduced so far.

SIP No. 9
Tape 2 - Work Sheet

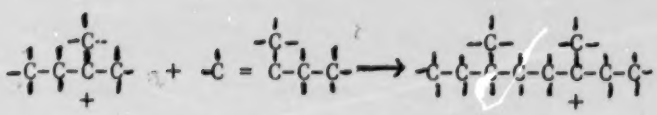
Assignment No. 6

Curious Chloe was asked to write the step by step mechanism for the acid catalyzed reaction of 2-methyl butene with 2-methyl butane. Her answer is given below. Supply all the necessary corrections.

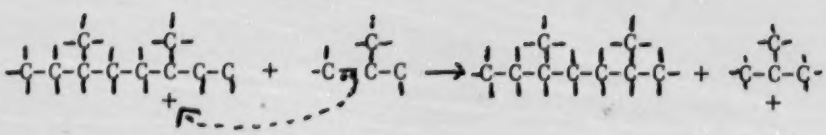
Step 1.



Step 2.



Step 3.



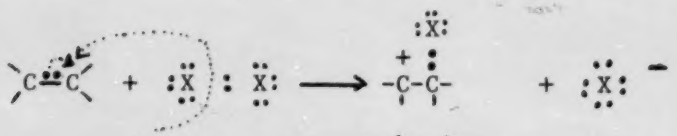
Assignment No. 7

Write the step by step mechanism and the overall reaction for the acid catalyzed reaction of 2-methyl propene and butane.

SIP No. 9
Tape 2 - Worksheet

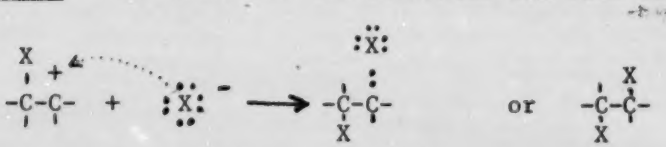
Example No. 3 - Mechanism for the halogenation reaction

Step 1 - Formation of the carbonium ion (addition of the electrophile to the double bond)



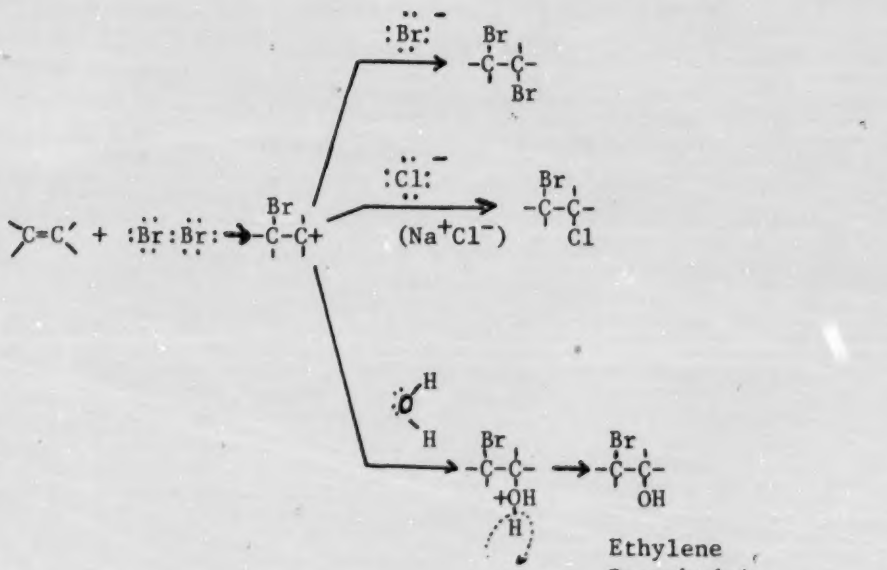
carbonium ion

Step 2 - Reaction of the carbonium ion with the nucleophile



vicinal dihalide

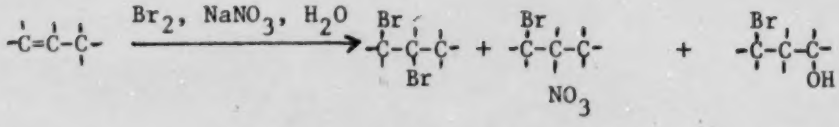
Example No. 4



Ethylene Bromohydrin (1-bromo-2-ethanol)

SIP No. 9
Tape 2 - Worksheet

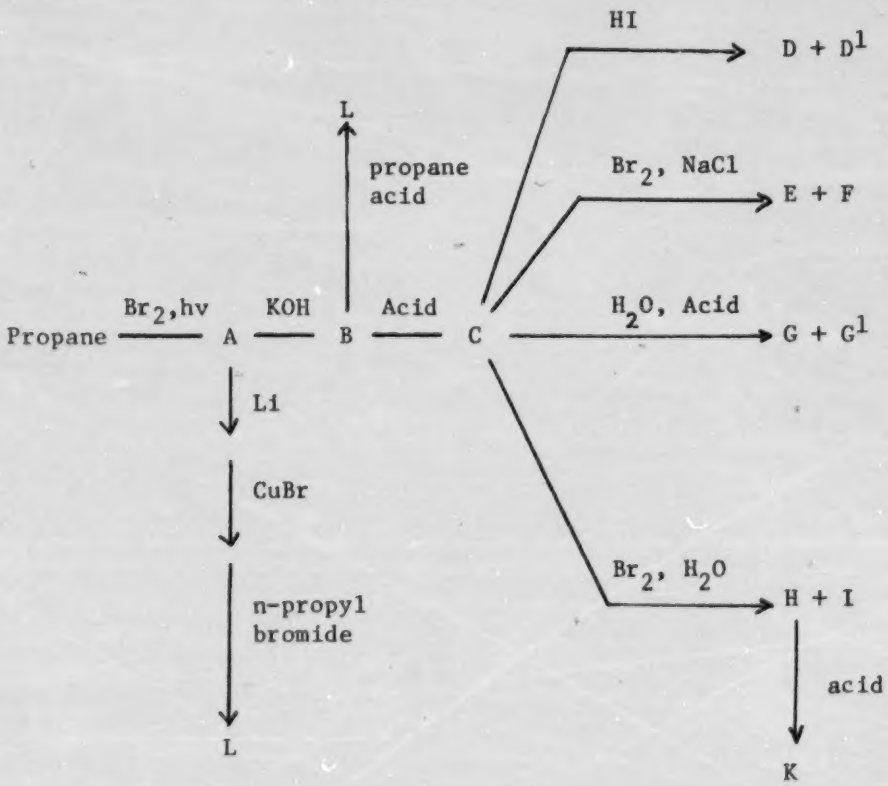
Example No. 5



Propylene
Bromo Hydrin
1-bromo-2-propanol

Assignment No. 8

Identify (draw the structure and name) compounds A through L in the reaction sequence below.



SIP No. 9
Tape 2 - Worksheet

Assignment No. 9

Write all the steps in the laboratory synthesis of:

a) 2-iodo-2,4,4-trimethyl pentane and b) 3-bromo-2,4,4-trimethyl-2-pentanol from isobutane.

Assignment No. 10

Apple growers could prevent spoilage of their fruit by circulating air from the containers and bubbling through bromine water. What kind of organic compounds will be removed in this process: saturated, or unsaturated?

Self Instructional Package No. 9
Tape 2 - Answer Sheet

ALKENES - REACTIONS

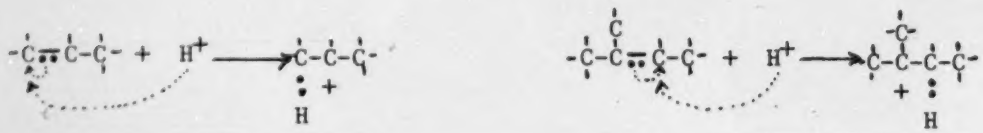
DIMERIZATION, ALKYLATION AND HALOGENATION

Assignment No. 1

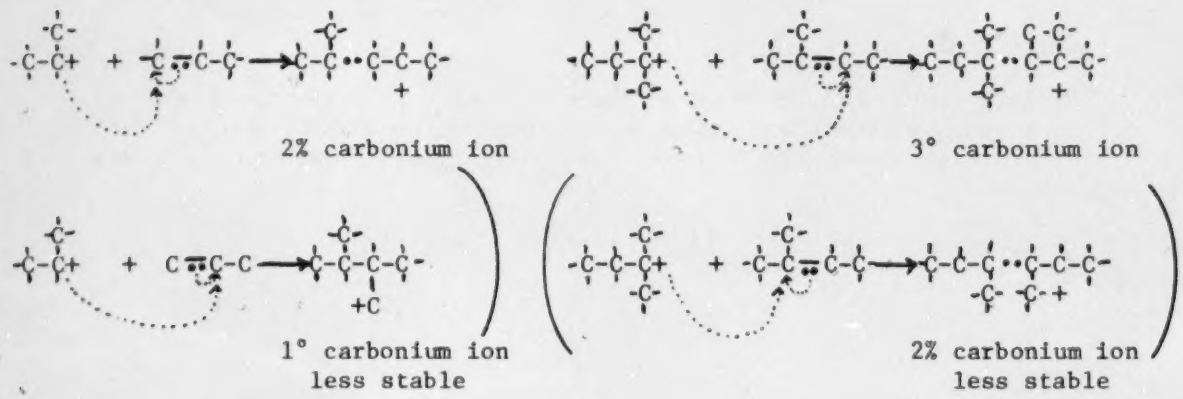
Dimerization of Propene

Dimerization of 2-methyl-2-butene

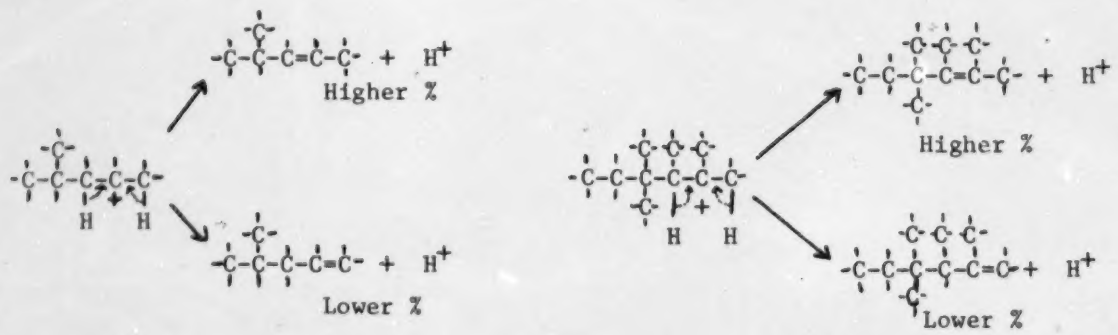
Step 1 - Formation of the carbonium ion



Step 2 - Addition of the carbonium ion to the alkene



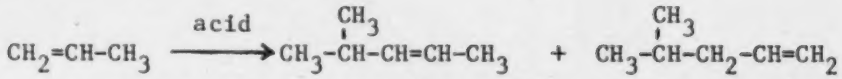
Step 3 = Loss of H^+



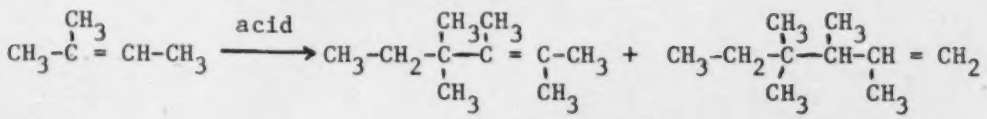
SIP No. 9
Tape 2 - Answer Sheet

Overall Reactions

1. Dimerization of propene



2. Dimerization of 2-methyl-2-butene



Assignment No. 2

a) 2-methyl-1-butene $\xrightarrow{\text{acid}}$ 3,4,4-trimethyl-2-hexene

b) 2-butene $\xrightarrow{\text{acid}}$ 3,4-dimethyl-2-hexene + 3,4-dimethyl-3-hexene + 3,4-dimethyl-1-hexene

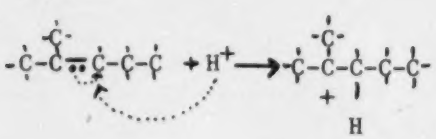
c) 1-butene $\xrightarrow{\text{acid}}$ 5-methyl-2-heptene + 5-methyl-3-heptene

d) 2-methyl propene $\xrightarrow{\text{acid}}$ 2,4,4-trimethyl-2-pentene + 2,4,4-trimethyl-1-pentene

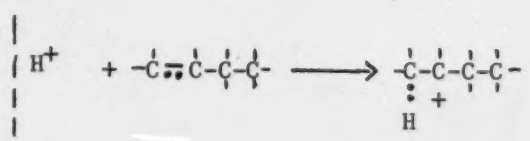
Assignment No. 3

Correct Mechanisms:

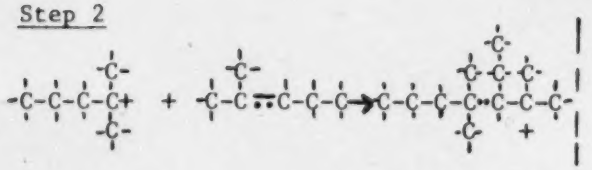
Step 1



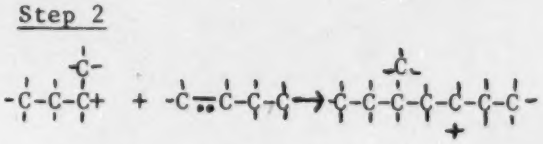
Step 1



Step 2



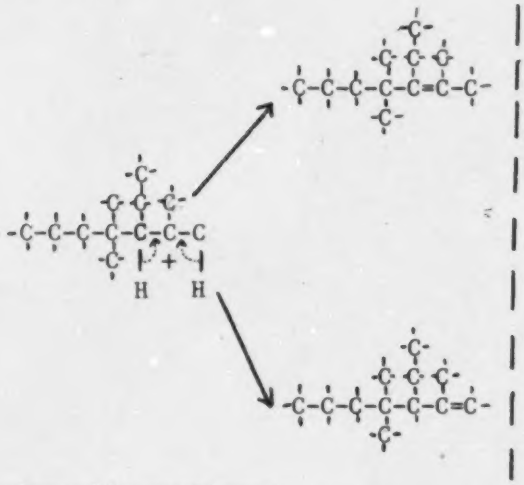
Step 2



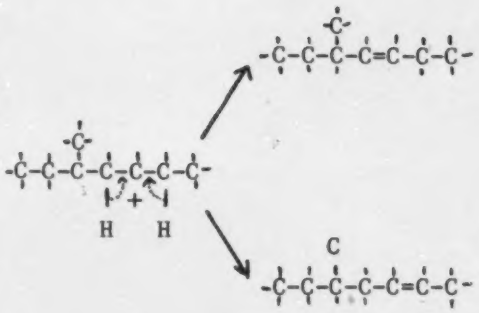
SIP No. 9
Tape 2 - Answer Sheet

Assignment No. 3 (continued)

Step 3



Step 3



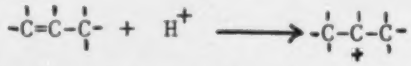
Overall reactions:

2-methyl-pentene $\xrightarrow{\text{acid}}$ 2,3,4-trimethyl-3-ethyl-2-heptene + 2,4,4-trimethyl-3-ethyl-1-heptene

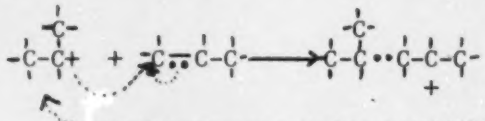
1-butene $\xrightarrow{\text{acid}}$ 5-methyl-3-heptene + 5-methyl-2-heptene

Assignment No. 4

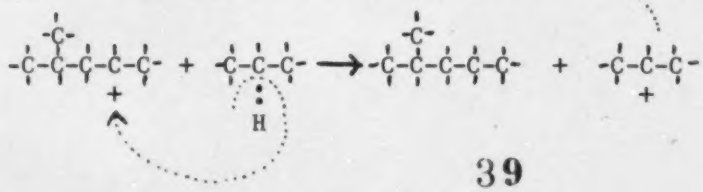
Step 1 - Formation of the carbonium ion



Step 2 - Reaction of the carbonium ion with alkene to yield a new carbonium ion



Step 3 - Abstraction of the hydride ion



SIP No. 9
Tape 2 - Answer Sheet

Assignment No. 5

A carbonium ion can:

a) lose a hydrogen positive ion to form an alkene.

b) abstract a hydride ion from an alkane.

c) add to another alkene to form a new carbonium ion.

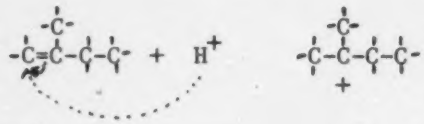
d) rearrange to form a more stable carbonium ion.

e) combine with a negative ion or any nucleophile.

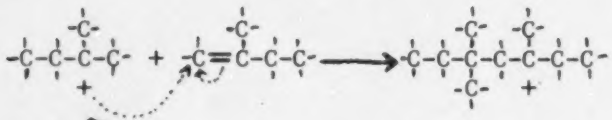
Assignment No. 6

Correct Mechanism:

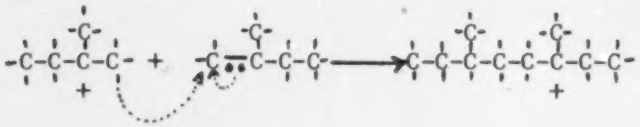
Step 1



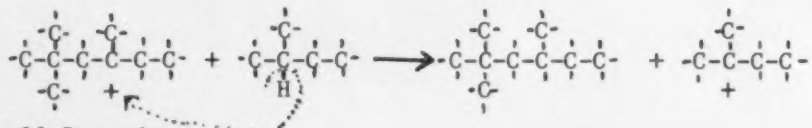
Step 2



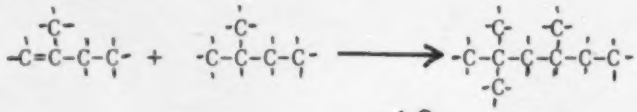
NOT



Step 3



Overall Reaction:

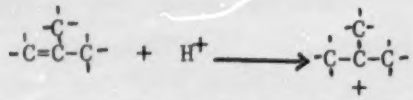


40

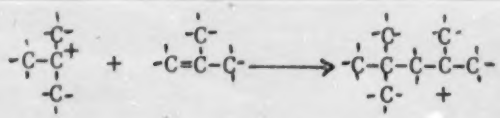
SIP No. 9
Tape 2 - Answer Sheet

Assignment No. 7

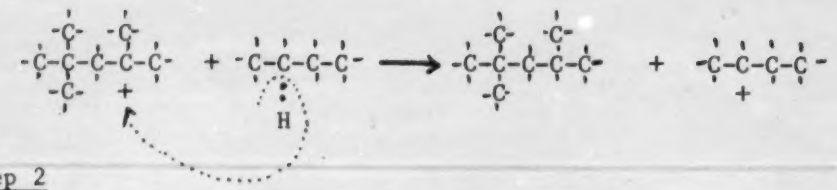
Step 1



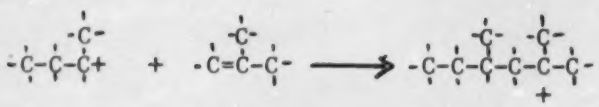
Step 2a



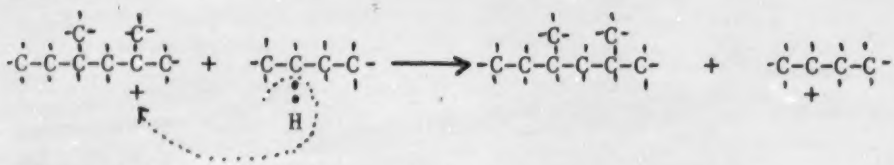
Step 3a



Step 2

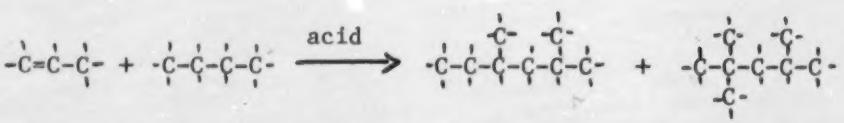


Step 3



Steps 2,3 2,3 2,3

Overall Reaction:

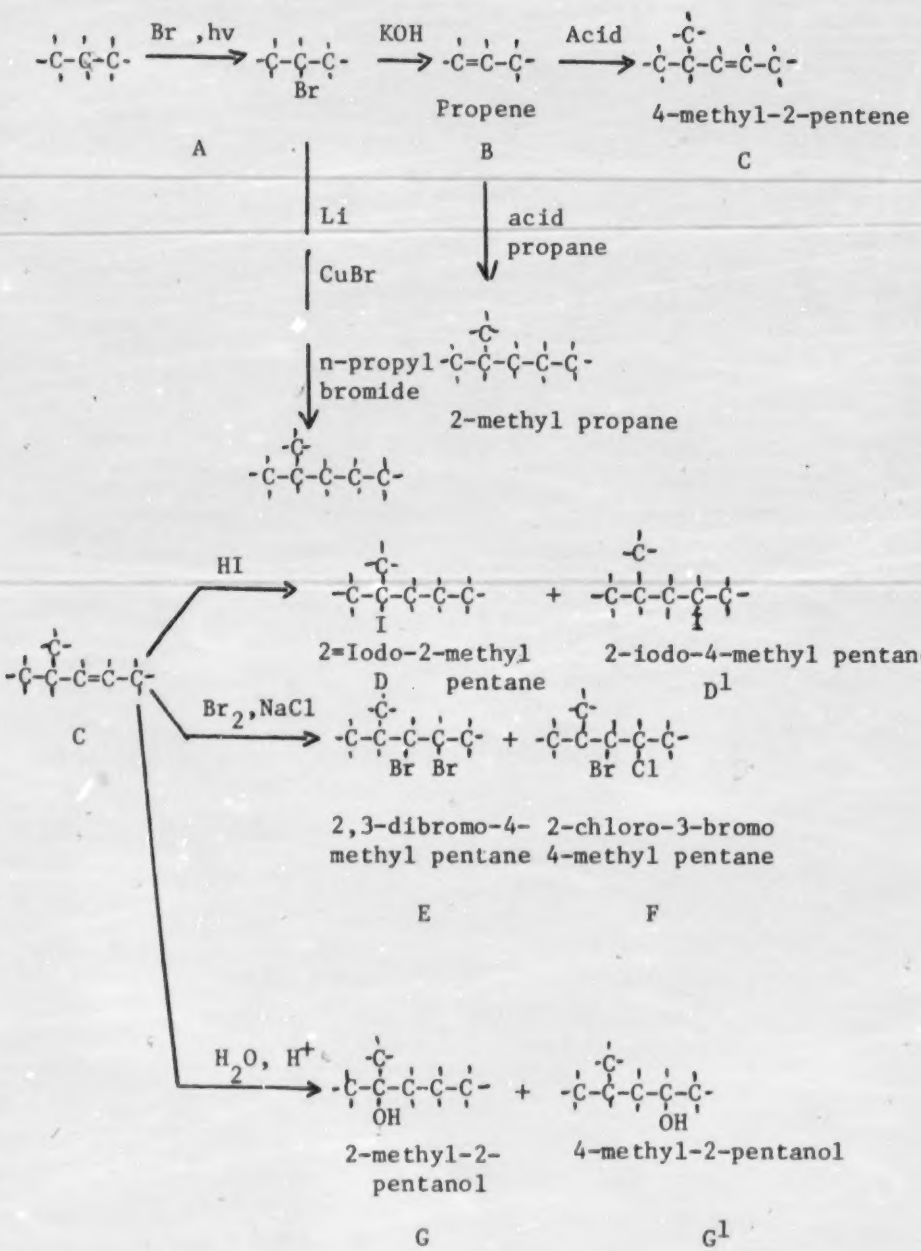


Major Product Low %

41

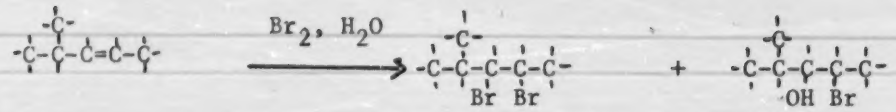
SIP No. 9
Tape 2 - Answer Sheet

Assignment No. 8



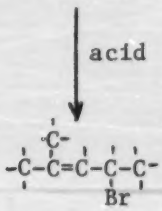
SIP No. 9
Tape 2 - Answer Sheet

Assignment No. 8 (continued)



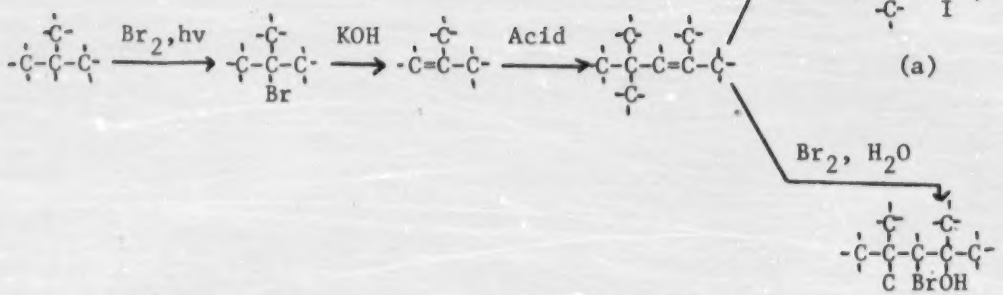
2,3-dibromo
4-methyl pentane

2-bromo-4-methyl
3-pentanol



4-bromo-2-methyl
2-pentene

Assignment No. 9



Assignment No. 10

Unsaturated (addition reaction of bromine to the double bond).

Self Instructional Package No. 9
Form D - Progress Check Evaluation

ALKENES - REACTIONS I

ELECTROPHILIC ADDITION REACTIONS

Identify the statements below as true or false by placing a T or an F in the space provided.

1. _____ The major product of a dimerization reaction is a symmetrical alkene.

2. _____ The major product of the alkylation reaction is a larger alkene.

3. _____ A halohydrin is formed in the reaction of an alkene with water and halogen.

4. _____ In a dimerization reaction alkene serves as an electrophile and a nucleophile.

5. _____ Alkylation reaction is an example of the intramolecular hydride shift.

6. _____ In the addition of HI to isobutene, H will add to the carbon that holds less hydrogens.

7. _____ Reaction of an alkene with concentrated sulfuric acid followed by dilution with water and heating will yield an alcohol.

8. _____ Isobutene is less reactive toward addition of sulfuric acid than butene.

9. _____ 2-methyl-2-pentene is more reactive toward addition of hydrogen iodide than 2-pentene.

10. _____ 2-methyl-2-butene is less reactive in a hydration reaction than 2,3-dimethyl-2-butene.

11. _____ In an electrophilic addition hydrogen positive ion adds to the alkene and causes the following changes:

    a) homolyte cleavage of the π bond in the alkene

    b) heterolytic cleavage of the π bond in the alkene

    c) it abstracts an electron of the π bond

    d) it abstracts both electrons of the π bond.

12. _____ In the hydration reaction carbonium ion reacts with

a) water

b) hydroxide anion

c) acid

d) acidic anion

13. _____ When isobutene reacts with bromine in aqueous solution the folloiwng product or products are formed:

a) 1,2-dibromo-2-methyl propane

b) 1-bromo-2-methyl-2-propanol

c) 1-bromo-2-methyl-1-propanol

d) 2-bromo-1-methyl-1-propanol

14. _____ When 2-methyl-2-butene reacts with bromine in aqueous solution in presence of sodium iodide the following product or products are formed:

a) 3-bromo-2-iodo-2-methyl butane

b) 3-bromo-2-methyl-2-propanol

c) 2-methyl-2,3-dibromo butane

d) 2-bromo-3-iodo-2-methyl butane

e) 3-bromo-2-methyl-2-butanol

15. _____ The following statements about a halohydrin are correct:

a) It is a compound that contains a halogen and an OH group on the vicinal carbon atoms

b) It is a compound that contains a halogen and an OH group

c) It is produced when halogen is added to an alkene in presence of acid

d) It is the result of the reaction of an alkene with halogen in aqueous medium

SIP No. 9
Form D - Progress Check Evaluation

16. _____ The following statements about the alkylation reaction are true.

a) It is a chain reaction

b) A new carbonium ion is generated in the last step of the reaction

c) The reaction results in a formation of an alkene

d) The reaction is essentially an addition of an alkene to an alkene.

17. _____ The product or products obtained in the dimerization of 2-butene is/are:

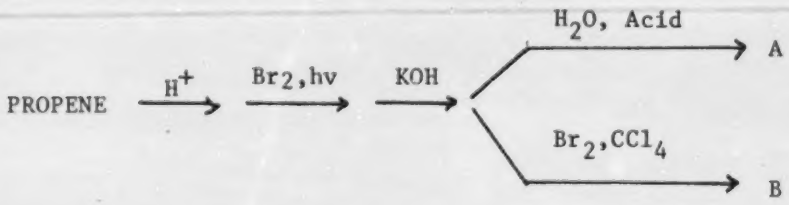
a) 3,4-dimethyl-3-hexene

b) 4-octene

c) 3,4-dimethyl-2-hexene

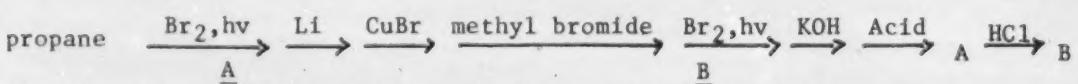
d) 3,4-dimethyl-1-hexene

18. _____ Compounds A and B obtain in the multi-step synthesis scheme below are:



	A	B
a)	2-methyl-3-pentanol	2,3-dibromo-2-methyl pentane
b)	2-propanol	1,2-dibromo propane
c)	2-methyl-2-butanol	2,3-dibromo-2-methyl butane
d)	2-methyl-2-pentanol	2,3-dibromo-2-methyl pentane

19. _____ Identify compounds A and B in the multi-step synthesis scheme below.



a)	2,4,4-dimethyl-2-pentene	3-chloro-2,4,4-trimethyl pentane
b)	2,4-dimethyl-2-pentene	2-chloro-2,4-dimethyl-2-pentene
c)	2,4,4-dimethyl-2-pentene	2-chloro-2,4,4-trimethyl pentane
d)	2-methyl-2-pentene	2-chloro-2-methyl pentane

20. _____ Identify <u>all</u> the correct pathways for the synthesis of 2,3-dimethyl-2-butanol from propane.

Br_2,hv, Na, Br_2,hv, H^+, H_2O,H^+

Br_2,hv, Na, Br_2,hv, KOH, H_2O,H^+

Br_2,hv, Li, CuBr, Isopropyl Bromide, Br_2,hv, KOH, H_2O,H^+

Br_2,hv, Na, Br_2,hv, KOH, H_2SO_4 conc., H_2O, heat

21. _____ The correct sequence of reagents required for the preparation of 2-iodo-2-methyl pentane from propane is/are:

a) Br_2,hv, KOH, Li, CuBr, isopropyl bromide, Br_2,hv, KOH, HI

b) Br_2,hv, KOH, acid, HI

c) Br_2,hv, Li, CuBr, n-propyl bromide, Br_2,hv, KOH, HI

d) Br_2,hv, Na, Br_2,hv, KOH, HI

Self Instructional Package No. 9
Form B^1 - Answer Sheet

ALKENES - REACTIONS I

ELECTROPHILIC ADDITION REACTIONS

1. T
2. F
3. T
4. F
5. F
6. T
7. T
8. F
9. T
10. T
11. T
12. T
13. F
14. b, c,
15. c, d,
16. a, c, d,
17. c,
18. d,
19. d,
20. b,
21. b, c, d,

Self Instructional Package No. 9
Form D' - Answer Sheet

ALKENES - REACTIONS I

ELECTROPHILIC ADDITION REACTIONS

1. F
2. F
3. T
4. F
5. F
6. F
7. T
8. F
9. T
10. T
11. b, d
12. a
13. a, b
14. a, c, e
15. a, d
16. a, b, d
17. a, c, d
18. d
19. c
20. b, c, d
21. b, c